
Carl Frisbie
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03/31/2016
Final Report
# Design, Synthesis, and Characterization of High Performance Polymer Electrolytes for Printed Electronics and Energy Storage

## Abstract

This is the final report for FA9550-12-1-0067. Principal investigators Frisbie and Lodge developed novel gel electrolytes for use in printed electronics and energy storage. This project produced 11 peer reviewed papers and results in the training of 3 graduate students and two postdoctoral fellows. The main innovations were the development of ion gels, materials that combine an ionic liquid with a gelating block copolymer to give mechanical strength. Judicious choice of the block polymer resulted in functional ion gels that displayed high toughness, good elasticity, and high ionic conductivity simultaneously. In addition, by adding redox-active reagents to the gels additional functions such as electrochromism and electrochemiluminescence could be achieved. Display elements based on electrochromic gels, in particular, were bendable, low voltage and low power.

## Subject Terms

- electrolyte
- organic
- polymer
Final Report for FA 9550 – 12 – 1 – 0067

Title: Design, Synthesis, and Characterization of High Performance Polymer Electrolytes for Printed Electronics and Energy Storage

Project Period: 4/1/12 – 9/30/15

Expenditures: $585,379

Principal Investigators:
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Abstract
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Project Goal
The overarching goal of this project was to develop a new generation of high performance polymer electrolytes for applications in electronics, electrochromic displays, and energy storage. The proliferation of portable, wireless devices for mobile communications, chemical detection, and global positioning has made high-performance, light-weight power sources of increasing importance to the US military. Polymer electrolyte membranes, which isolate electrodes while allowing passage of substantial ionic currents, are critical materials for
energy conversion and storage devices – including supercapacitors, lithium ion batteries, and fuel cells – that power portable electronics. Likewise, efforts to integrate electronics into flexible, stretchable, conformal, impact-resistant and wearable formats for the warfighter are driving development of thin film polymer electrolytes for printed batteries, capacitors, circuits, and sensors. In short, polymer electrolytes are ubiquitous in energy storage and electronics applications that are central to US security, and improvement of these materials can greatly enhance device performance and national defense capabilities. Importantly, while the specific requirements for polymer electrolytes vary with application, the basic challenge is universal, namely to achieve maximum ionic conductivity while separately controlling mechanical and thermal properties (e.g., elasticity, toughness, stability) of the polymer electrolyte films.

**Strategy**
Principal investigators Frisbie and Lodge designed, synthesized and characterized new polymer electrolytes based on high conductivity ionic liquids (ILs) and self-assembling block copolymers, Figure 1. In these novel composites, referred to as ‘ion gels’, the block polymers provided a solid, rubbery or glassy network with tunable mechanical and thermal properties, while the ionic liquids provided high conductivity, wide electrochemical stability windows, chemical inertness and thermal stability. This materials design effort built on prior collaborative work by the PIs in which they successfully created ion gels for printed electronics applications. Physically cross-linked, reversible ion gels exhibit among the highest ionic conductivities (>10^{-2} S/cm) of known solvent-free, non-aqueous polymer electrolyte systems. Furthermore, the mechanical and thermal properties can be conveniently tuned; for example, ion gels can have high elasticity and toughness, and they can be “thermoreversible”, allowing solvent free, melt-state processing strategies.

**Accomplishments**
This project resulted in ten publications in the peer-reviewed literature. Highlights are outlined below.

1. **Synergistic increase in strength and conductivity of ion gels**
Lodge, Frisbie and their student collaborators successfully synthesized a new triblock polymer, polystyrene-b-poly(ethyl acrylate)-b-polystyrene (SEAS), which is compatible
with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) ionic liquid. The SEAS triblock is hydrophobic and has a low glass transition temperature midblock. The resulting SEAS ion gels demonstrated significantly less drop in ionic conductivity as polymer concentration increased in comparison to prior polystyrene-polymethylmethacrylate-polystyrene (SMS) ion gels. In addition, the SEAS ion gels are more stable under humidity in comparison to hydrophilic polystyrene-polyethylene oxide-polystyrene (SOS) ion gels, which is advantageous to avoid water uptake in applications. Shortening the EA midblock length improved the stiffness of the ion gel by tightening and promoting bridging between microphase separated, glassy polystyrene micelles at constant polymer concentration while achieving a synergistic improvement in ionic conductivity. Despite the fact that, at constant polymer concentration, the ion-insulating polystyrene phase fraction increased as the midblock size shortened, the ionic conductivity of the ion gels improved because the ionic liquid fraction in the ion-conducting phase also increased. Thus, using appropriately designed SEAS block polymers, the PIs were able to achieve a synergistic increase in both the modulus and ionic conductivity of SEAS based ion gels, Figure 2.

In an alternative strategy, the PIs created a novel ABA triblock system that can be chemically cross-linked in a second annealing step, thereby providing greatly enhanced toughness. The ABA triblock was a poly(styrene-\textit{b}-ethylene oxide-\textit{b}-styrene) polymer in which about 25 mol % of the styrene units have a pendant azide functionality. After self-assembly of 10 wt % triblock in the ionic liquid [EMI][TFSA], the styrene domains were cross-linked by annealing at elevated temperature for ca. 20 min. The high ionic conductivity (ca. 10 mS/cm) of the physical ion gels was preserved in the final product, while the tensile strength is increased by a factor of 5.

The above findings lead to these publications:

2. Electrochromic functionality in ion gels for printed displays

Frisbie and Lodge also examined the use of redox active additives to the ion gels to enhance their functionality. In particular, they developed ionic-liquid soluble electrochromic salts based on viologen that were capable of showing the full spectrum of display colors (red, green and blue) upon electrochemical reduction. These redox dies were added to gels that were sandwiched between transparent ITO electrodes on plastic. Application of small voltages (e.g., 2V) resulted in the device changing color. By patterning the gels, colorful printed displays operating at low voltage were created, Figure 3.

![Coloration and Bleaching](image)

**Figure 3.** Printed display based on electrochromic ion gels.

In a variation on this theme, electrochemiluminescent dyes were added to the gels. In this case, application of a voltage resulted in a luminescent gel which is also of potential importance for printed displays.

This work resulted in these publications:


Full List of Publications:


1. Report Type
Final Report

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Primary Contact Phone Number
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Organization / Institution name
University of Minnesota

Grant/Contract Title
The full title of the funded effort.

Grant/Contract Number
AFOSR assigned control number. It must begin with “FA9550” or “F49620” or “FA2386”.
FA9550-12-1-0067

Principal Investigator Name
The full name of the principal investigator on the grant or contract.
Dan Frisbie

Program Manager
The AFOSR Program Manager currently assigned to the award
Charles Lee

Reporting Period Start Date
04/01/2012

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09/30/2015

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Archival Publications (published) during reporting period:


Changes in research objectives (if any):

None

Change in AFOSR Program Manager, if any:

None

Extensions granted or milestones slipped, if any:

None

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

DISTRIBUTION A: Distribution approved for public release.
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Report Document

Report Document - Text Analysis

Appendix Documents

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